

1,009,914

# PATENT SPECIFICATION

NO DRAWINGS

1,009,914



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Int. Cl.:—C 07 c, f // A 01 n, C 08 f, C 10 m

## COMPLETE SPECIFICATION

### Phosphorus- and Nitrogen-containing Compositions and Lubricating Compositions containing them

We, THE LUBRIZOL CORPORATION, a Corporation organized and existing under the laws of the State of Ohio, United States of America, of Box 3057, Euclid Station, Cleveland 17, Ohio, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

5

This invention concerns phosphorus- and nitrogen-containing compositions, i.e. mixtures of compounds containing phosphorus and nitrogen, a process of preparing them and lubricating compositions containing them.

10 Although organic phosphorus and nitrogen compounds are quite effective for use as plasticizers, pesticides, weed killers, rust-inhibitors, corrosion-inhibitors, detergents, etc., they have not, generally, found wide application because of their susceptibility to thermal degradation. There is, accordingly, a great deal of interest in processes for preparing thermally stable organic phosphorus and nitrogen compounds.

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15 In our copending Patent Application No. (1,009,913) 27021/62, there is described and claimed a process for preparing a phosphorus- and nitrogen-containing composition comprising forming an acidic intermediate by the reaction of a hydroxy-substituted triester of a phosphorothioic acid with an inorganic phosphorus acid, phosphorus oxide or phosphorus halide, and neutralizing a substantial portion of said acidic intermediate with an amine. That application also contains claims 20 to the product of this process and a lubricating composition containing the product.

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20 We have now found it to be desirable to use a hydroxy-substituted amine in the process defined above.

20

25 In accordance with this invention, a process for preparing a phosphorus- and nitrogen-containing composition thus comprises forming an acidic intermediate by the reaction of a hydroxy-substituted triester of a phosphorothioic acid with an inorganic phosphorus acid, phosphorus oxide, or phosphorus halide, and neutralizing a substantial portion of said acidic intermediate with a hydroxy-substituted amine.

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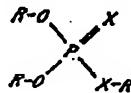
The term 'inorganic phosphorus halide' as used herein is intended to include phosphorus oxyhalides and phosphorus thiohalides.

30 The term 'substantially hydrocarbon radical' as used herein means a hydrocarbon radical containing no more than one polar group, for example chlorine, as a substituent.

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The hydroxy-substituted triesters of phosphorothioic acids useful in this invention include principally those having the structural formula

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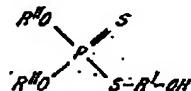
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wherein R is selected from the class consisting of substantially hydrocarbon radicals and hydroxy-substituted substantially hydrocarbon radicals, at least one of the R radicals being a hydroxy-substituted substantially hydrocarbon radical, and X is sulfur or oxygen, at least one of the X radicals being sulfur. The substantially hydrocarbon radicals include aromatic, aliphatic, and cycloaliphatic radicals such as aryl, alkyl, aralkyl, alkaryl, and cycloalkyl radicals. Such radicals may contain a polar substituent such as chloro, bromo, iodo, alkoxy, aryloxy, nitro, keto, or aldehydo group but, as indicated above, there should be no more than one such polar group in a radical.

Specific examples of the substantially hydrocarbon radical are methyl, ethyl, isopropyl, secondary-butyl, isobutyl, n-pentyl, dodecyl, polyisobutene radical (molecular weight of 1500), cyclohexyl, cyclopentyl, 2-heptyl-cyclohexyl, phenyl, naphthyl, xenyl, p-heptyl-phenyl, 2,6-di-tertiary-butylphenyl, benzyl, phenylethyl, 3,5-dodecyl-phenyl, chlorophenyl, alpha-methoxy-beta-naphthyl, p-nitro-phenyl, p-phenoxy-phenyl, 2-bromoethyl, 3-chloro-cyclohexyl, and polypropylene (molecular weight of 300)-substituted phenyl radical.

The hydroxy-substituted substantially hydrocarbon radicals include principally the above-illustrated substantially hydrocarbon radicals containing a hydroxy group. Those having less than about 8 carbon atoms are preferred because of the convenience in preparing such hydroxy-substituted triesters. Examples of such radicals are hydroxymethyl, hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxycyclohexyl, 2-hydroxycyclopentyl, 2-hydroxy-1-octyl, 1-hydroxy-3-octyl, 1-hydroxy-2-octyl, 2-hydroxy-3-phenyl-cyclohexyl, 1-hydroxy-2-phenylethyl, 2-hydroxy-1-phenylethyl, 2-hydroxy-1-p-tolyethyl, and 2-hydroxy-3-butyl radicals. Other hydroxy-substituted substantially hydrocarbon radicals are exemplified by 2,5-dihydroxyphenyl, alpha-hydroxy-beta-naphthyl, 3-hydroxy-4-dodecyl, 3-hydroxy-6-octadecyl, and p-(p-hydroxyphenyl)-phenyl radicals.

A preferred class of the hydroxy-substituted triesters comprises those having the structural formula

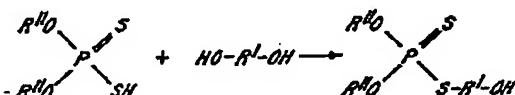
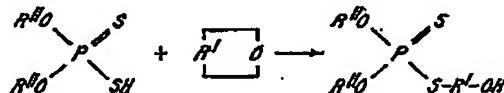


wherein R<sup>11</sup> is a substantially hydrocarbon radical illustrated above and R<sup>1</sup> is a bivalent substantially hydrocarbon radical such as an alkylene or aryleno radical derived from the previously illustrated substantially hydrocarbon radicals.

Preferred processes according to the invention are those in which:—

- (a) R<sup>11</sup> and R<sup>1</sup> in the formula are aliphatic radicals.
- (b) R<sup>11</sup> in the formula is an alkyl radical and R<sup>1</sup> in the formula is an alkylene radical.
- (c) R<sup>11</sup> in the formula is an aliphatically-substituted aromatic radical and R<sup>1</sup> of the formula is a substantially aliphatic radical.
- (d) R<sup>11</sup> in the formula is an alkaryl radical and R<sup>1</sup> in the formula is an alkylene radical.

A convenient method for preparing such esters involves the reaction of a phosphorodithioic acid with an epoxide or a glycol. Such reaction is known in the art. The following equations are illustrative of the reaction.



wherein



is an epoxide and HO—R¹—OH is a glycol.

For reasons of economy aliphatic epoxides having less than about 8 carbon atoms and styrene oxides are preferred for use in the above process. Especially useful epoxides are exemplified by ethylene oxide, propylene oxide, styrene oxide, alpha-methylstyrene oxide, p-methylstyrene oxide, cyclohexene oxide, cyclopentene oxide, dodecene oxide, octadecene oxide, 2,3-butene oxide, 1,2-butene oxide, 1,2-octene oxide, 3,4-pentene oxide, and 4-phenyl-1,2-cyclohexene oxide. Glycols include both aliphatic and aromatic di-hydroxy compounds. The latter are exemplified by hydroquinone, catechol, resorcinol, and 1,2-dihydroxynaphthalene. Aliphatic glycols are especially useful such as ethylene glycol, trimethylene glycol, tetramethylene glycol, hexamethylene glycol, propylene glycol, pentylene glycol, decamethylene glycol, diethylene glycol, triethylene glycol, and pentaethylene glycol.

Another convenient method for preparing the hydroxy-substituted triesters comprises the addition of a phosphorodithioic acid to an unsaturated alcohol such as allyl alcohol, cinnamyl alcohol, or oleyl alcohol such as is described in U.S. Patent 2,528,732. Still another method involves the reaction of a metal phosphorothioate with a halogen-substituted alcohol. This method is described in U.S. Reissue Patent 20,411.

The phosphorodithioic acids from which the hydroxy-substituted triesters can be derived are likewise well-known. They are prepared by the reaction of phosphorus pentasulfide with an alcohol or a phenol. The reaction involves 4 moles of the alcohol or phenol per mole of phosphorus pentasulfide and may be carried out within the temperature range from about 50°C to about 200°C. Thus the preparation of O,O'-di-n-hexylphosphorodithioic acid involves the reaction of phosphorus pentasulfide with 4 moles of n-hexyl alcohol at about 100°C for about 2 hours. Hydrogen sulfide is liberated and the residue is the defined acid. The preparation of the phosphoromonothioic acid may be effected by treatment of the corresponding phosphorodithioic acid with steam. Phosphorothioic acids and phosphorotetrathioic acids can be obtained by the reaction of phosphorus pentasulfide with mercaptans or mixtures of mercaptans and alcohols.

The reaction of phosphorus pentasulfide with a mixture of phenols or alcohols (e.g., isobutanol and n-hexanol in 2:1 molecular weight ratio) results in phosphorodithioic acids in which the two organic radicals are different. Such acids likewise are useful herein.

The inorganic phosphorus reagent useful in the reaction with the hydroxy-substituted triesters of phosphorothioic acids is preferably phosphorus pentoxide. Other phosphorus oxides such as phosphorus trioxide and phosphorus tetroxide likewise are useful. Also useful are phosphorus acids, and phosphorus halides. They are exemplified by phosphoric acid, pyrophosphoric acid, metaphosphoric acid, hypo-phosphoric acid, phosphorous acid, pyrophosphorous acid, metaphosphorous acid, hypo-phosphorous acid, phosphorus trichloride, phosphorus tribromide, phosphorus pentachloride, monobromophosphorus tetrachloride, phosphorus oxychloride, phosphorus thiocloride, and phosphorus triiodide.

The reaction of the hydroxy-substituted triesters of phosphorothioic acids with the inorganic phosphorus reagent results in an acidic product. The chemical constitution of the acidic product depends to a large measure on the nature of the inorganic phosphorus reagent used. In most instances the product is a complex mixture the precise composition of which is not known. It is known, however, that the reaction involves the hydroxy radical of the triester with the inorganic phosphorus reagent. In this respect the reaction may be likened to that of an alcohol or a phenol with the inorganic phosphorus reagent. Thus, the reaction of the hydroxy-substituted triester with phosphorus pentoxide is believed to result principally in acidic phosphates, i.e., mono- or di-esters of phosphoric acid in which the ester radical is the residue obtained by the removal of the hydroxy radical of the phosphorothioic triester reactant. The product may also contain phosphonic acids and phosphinic acids in which one or two direct carbon-to-phosphorus linkages are present.

The acidic product of the reaction between the hydroxy-substituted triester

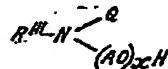
with phosphorus oxyhalide or phosphoric acid is believed to result in similar mixtures of acidic phosphates, phosphonic acids, and/or phosphinic acids. On the other hand the reaction of the hydroxy-substituted triester with phosphorus trichloride or phosphorous acid is believed to result principally in acidic organic phosphites. Still other products may be obtained from the use of other inorganic phosphorus reagents illustrated previously. In any event, the product is acidic and as such is useful as the intermediate for the preparation of the neutralized products of this invention.

Usually, from 2 moles to 5 moles of the triester is used for each mole of the inorganic phosphorus reagent. The preferred proportion of the triester is about 3-4 moles for each mole of the phosphorus reagent. The use of amounts of either reactant outside the limits indicated here results in excessive unused amounts of the reactant and is ordinarily not preferred.

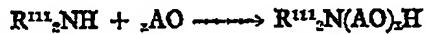
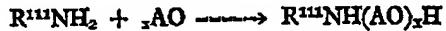
The reaction of the hydroxy-substituted triester with the inorganic phosphorus reagent to produce the acidic intermediate can be effected simply by mixing the two reactants at a temperature preferably above room temperature, particularly above 50°C. A higher temperature such as 100°C or 150°C may be used but ordinarily is unnecessary.

The hydroxy amines useful for neutralizing the acidic intermediate may be aliphatic amines, aromatic amines, cycloaliphatic amines, or heterocyclic amines. Amines having from 4 to 30 aliphatic carbon atoms are preferred. Useful amines include such as ethanolamine, diethanolamine, triethanolamine, isopropanolamine, para-aminophenol, 4 - amino - naphthol - 1, 8 - amino - naphthol - 1, beta - aminoalizarin, 2 - amino - 2 - ethyl - 1,3 - propanediol, 4 - amino - 4<sup>1</sup> - hydroxydiphenyl ether and 2 - amino - resorcinol.

Of the various available hydroxy-substituted amines which can be employed, a preference is expressed for hydroxy-substituted aliphatic amines, particularly those which conform for the most part to the formula



wherein R<sup>111</sup> is a substantially hydrocarbon radical as previously defined; A is a C<sub>1-5</sub> alkylene radical such as methylene, ethylene, propylene-1,2, trimethylene, butylene-1, 2, tetramethylene, amylene-1,3, and pentamethylene; x is 1-10, inclusive; and Q is hydrogen, (AO)<sub>x</sub>H or R<sup>111</sup>. The use of such hydroxy-substituted aliphatic amines in many instances imparts improved rust-inhibiting characteristics to the phosphorus- and nitrogen-containing compositions of this invention. Examples of such preferred hydroxy- substituted aliphatic amines include N - 4 - hydroxybutyl - dodecyl amine, N - 2 - hydroxyethyl - n - octylamine, N - 2 - hydroxypropyl dinonyl-amine, N,N - di - (3 - hydroxypropyl) - tert - dodecyl amine, N - hydroxytriethoxyethyl - tert - tetradecyl amine, N - 2 - hydroxyethyl - tert - dodecyl amine, N - hydroxy - hexapropoxypropyl - tert - octadecyl amine, and N - 5 - hydroxypentyl di - n - decyl amine. A convenient and economical method for the preparation of such hydroxy-substituted aliphatic amines involves the known reaction of an aliphatic primary or secondary amine with at least about an equimolecular amount of an epoxide, preferably in the presence of a suitable catalyst such as sodium methoxide, sodamide, or sodium metal.



In the above formulas, R<sup>111</sup>, x, and A are as previously defined. A particular preference is expressed for N - monohydroxyalkyl substituted mono-tertiary-alkyl amines of the formula tert-R-NHAOH, wherein tert-R is a tertiary-alkyl radical containing from 11 to 24 carbon atoms. In lieu of a single compound of the formula tert-R-NHAOH, it is often convenient and desirable to use a mixture of such compounds prepared, for example, by the reaction of an epoxide such as ethylene oxide, propylene oxide, or butylene oxide with a commercial mixture of tertiary-alkyl primary amines such as C<sub>11</sub>-C<sub>14</sub> tertiary-alkyl primary amines, and C<sub>16</sub>-C<sub>22</sub> tertiary-alkyl primary amines.

5        The neutralization of the acidic intermediate with the amine is in most instances exothermic and can be carried out simply by mixing the reactants at ordinary temperatures, preferably from about 0°C to about 200°C. The chemical constitution of the neutralized product of the reaction depends to a large extent upon the temperature. Thus, at a relatively low temperature, such as less than about 80°C, the product comprises predominantly a salt of the amine with the acid. At a temperature above about 100°C, the product may contain amides, amidines, or mixtures thereof. However, the reaction of the acidic intermediate with a tertiary amine results only in a salt.

10      The relative proportions of the acidic intermediate and the amines used in the reaction are preferably such that a substantial portion of the acidic intermediate is neutralized. The lower limit as to the amount of amine used in the reaction is based primarily upon a consideration of the utility of the product formed. In most instances, enough amine should be used as to neutralize at least about 50% of the acidity of the intermediate. For use as additives in hydrocarbon oils, substantially neutral products such as are obtained by neutralization of at least about 90% of the acidity of the intermediate are desirable, whereas for use as insecticides or rust-preventive agents for treatment of metals, products obtained by neutralizing as little as about 50% of the acidity of the intermediate are effective. Thus the amount of the amine used may vary within wide ranges depending upon the acidity desired in the product and also upon the acidity of the intermediate as determined by, for example, ASTM procedure designation D-664 or D-974.

15      The following examples are illustrative of the process for preparing the phosphorus- and nitrogen-containing compositions of this invention.

20      EXAMPLE 1  
25      2292 grams (12 moles) of a commercial mixture of C<sub>11</sub> to C<sub>14</sub> tertiary-alkyl primary amines having an average molecular weight of 191 is placed in a reaction vessel and heated to 170°C. Sodium metal catalyst (0.6 gram) is added and then 528 grams (12 moles) of ethylene oxide is introduced into the reaction vessel over a period of 25 hours at 165°—175°C. Thereafter, the whole is stripped at 110°C/20 mm Hg, diluted with 500 ml. of benzene, water-washed, dried by azeotropic distillation, and filtered. The filtrate is the desired N - 2 - hydroxyethyl substituted amine mixture containing 6.02% nitrogen (theory, 5.96%) and having a neutral equivalent of 236 (theory, 235).

30      35      2330 grams (5 equivalents) of phosphorus pentoxide-treated hydroxypropyl O,O-di-(4-methyl-2-pentyl) phosphorodithioate prepared in a manner similar to that set forth in Example 1 of Application No. 27021/62 (1,009,913) is introduced into a reaction vessel and stirred. Thereupon, 1180 grams (5 equivalents) of the above-described N-2-hydroxyethyl substituted amine mixture is added dropwise over a period of 0.75 hour. An exothermic reaction causes the temperature to rise to 60°C. After all of the amine has been added, the whole is stirred for 2 hours. The resulting neutralized product is found to have a phosphorus content of 8.05%, a nitrogen content of 2.03%, a sulfur content of 10.16%, and a base number of 29 (bromphenol blue indicator).

40      45      EXAMPLE 2  
45      50      296 grams (4 moles) of isobutanol and 222 grams (1 mole) of phosphorus pentasulfide are stirred for 5 hours at 75°C to yield O,O<sup>1</sup> - di - isobutyl phosphorodithioic acid. Thereafter, 102 grams (1.76 moles) of propylene oxide is added over a period of 0.25 hour at 50°C to yield hydroxypropyl O,O<sup>1</sup> - di - isobutyl phosphorodithioate, which latter compound is stirred for 5 hours at 70°—80°C with 83 grams (0.59 mole) of phosphorus pentoxide to prepare an acidic phosphorus- and sulfur-containing intermediate having an acid number of 163 (phenolphthalein indicator).

55      55      A chemically equivalent amount (440 grams) of the N - 2 - hydroxyethyl substituted amine mixture described in Example 1 is added to the acidic phosphorus- and sulfur-containing intermediate over a period of 0.5 hour at 65°C. The resulting neutralized product is found to have a phosphorus content of 8.74%, a nitrogen content of 2.43%, a sulfur content of 11.19%, and a base number of 26 (bromphenol blue indicator).

60      60      The phosphorus- and nitrogen-containing compositions of this invention are useful as insecticides, corrosion-inhibitors, rust-inhibitors, anti-wear agents, etc. To illustrate, they may be incorporated in insecticidal emulsions or atomized sprays at concentrations ranging from about 0.01% to about 5% by weight.

The phosphorus- and nitrogen-containing compositions of this invention are especially effective as corrosion-inhibiting and extreme pressure additives in lubricating compositions. When used as lubricant additives they are added to the lubricating oil in a minor proportion by weight and those derived from phosphorothioic acids in which the ester radicals contain a total of at least about 7.6 aliphatic carbon atoms per phosphorus atom are preferred because of their greater oil-solubility and compatibility with other additives which may be present in the lubricant.

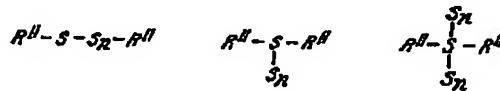
The lubricating oils in which the compositions of this invention are useful as additives may be of synthetic, animal, vegetable, or mineral origin. Ordinarily mineral lubricating oils are preferred by reason of their availability, general excellence, and low cost. For certain applications, oils belonging to one or the other three groups may be preferred. For instance, synthetic polyester oils such as didodecyl adipate and di-2-ethylhexyl sebacate are often preferred as jet engine lubricants. Normally the lubricating oils preferred will be fluid oils ranging in viscosity from about 40 Saybolt Universal Seconds at 100°F to about 200 Saybolt Universal Seconds at 210°F.

The concentration of the phosphorus- and nitrogen-containing compositions of this invention to be used in a lubricant depends primarily upon the type of oil used and the nature of the service to which the lubricating composition is to be subjected. In most instances the concentration will range from about 0.001% to about 10% by weight of the additive in a lubricant. More particularly, for example, a lubricant for gasoline internal combustion engines usually contains from about 0.05% to about 5% by weight of the additive, whereas a lubricant for diesel engines usually contains from about 0.1% to about 10% by weight of the additive. On the other hand, a lubricant for 2-cycle engines may contain as little as 0.01% or less by weight of the additive and a lubricant for power transmitting units such as gears or axles usually contains from about 0.5% to 5% by weight of the additive.

Other additives which can be used in conjunction with the phosphorus- and nitrogen-containing compositions of this invention in lubricants include principally detergents of both ashless and ash-containing types, supplemental corrosion-inhibiting agents, supplemental extreme pressure improving agents, rust-inhibiting additives, pour point depressant agent, viscosity index improving agents, antifoam agents, and oxidation-inhibiting agents.

A particularly effective combination of additives for use in lubricants for automobile transmissions, gears, or axles comprises the phosphorus- and nitrogen-containing composition of this invention together with a substantially hydrocarbon polysulfide. Lubricants containing such combination of additives are characterized by non-corrosiveness, improved stability against oxidative and thermal degradation, and the ability to provide effective lubrication in changing operating environments wherein shock load, high speed, and high torque demands are made both cyclically or in sequence on the lubricant.

The substantially hydrocarbon polysulfides which are especially useful for this purpose include principally aliphatic, cycloaliphatic, and aromatic disulfides, trisulfides, tetrasulfides, pentasulfides, or higher polysulfides. The term "polysulfide" as used herein designates compounds in which two substantially hydrocarbon radicals are joined to a group consisting of at least 2 sulfur atoms. Such polysulfides are represented, for the most part, by any of the structural formulas below



wherein  $R^{II}$  is a substantially hydrocarbon radical such as illustrated previously and  $n$  is an integer preferably less than 6. The nature of the linkage between the sulfur atoms is not clearly understood, although it is believed that such linkage may be described by a single covalent bond, a double bond, or a coordinate covalent bond.

Polysulfides preferred for use herein are alkyl polysulfides, cycloalkyl polysulfides, aralkyl polysulfides, aryl polysulfides, alkaryl polysulfides, or polysulfides having a mixture of such hydrocarbon radicals. The polysulfides containing at least about 6 carbon atoms per molecule have greater oil solubility and are generally preferred. Specific examples of such polysulfides are diisobutyl trisulfide, diisopentyl trisulfide, di-n-butyl tetrasulfide, dicyclopentyl disulfide, di-methylcyclohexyl tetrasulfide, di-2-ethylcyclopentyl disulfide, dipentyl trisulfide, beta-pinyl pentasulfide, dibenzyl trisulfide,

benzyl iso-octyl disulfide, diphenyl disulfide, cyclohexyl cyclopentyl trisulfide, alpha-butyl-beta-naphthyl trisulfide, bis(polyisobutene(molecular weight of 1000)-substituted phenyl) disulfide, di-tolyl disulfide, di-paraffin wax trisulfide, di-terpenyl disulfide, bis(o,p-diisopropylphenyl) tetrasulfide, didodecyl trisulfide, dibehenyl trisulfide, and isobutyl cyclohexyl tetrasulfide. Other polysulfides such as polar substituted polysulfides are exemplified by di(p-chlorobenzyl) disulfide, di-(omega-bromopentyl) tri-sulfide, di(p-butoxyphenyl) disulfide, and di(o-nitro-p-heptylphenyl) disulfide.

The preparation of the polysulfides may be accomplished by any of the various processes which are known and disclosed in the art including, for example, the reaction of a chlorohydrocarbon with an alkali metal polysulfide, the reaction of a mercaptan or a thiophenol with sulfur and/or sulfur halide, the reaction of saturated and unsaturated hydrocarbons with sulfur and/or sulfur halide, and the reaction of a hydrocarbon monosulfide with sulfur.

The concentration of the polysulfide in a lubricant is usually from about 0.05% to about 10% by weight.

Detergents useful in conjunction with the phosphorus- and nitrogen-containing composition in lubricants include normal or basic salts of petroleum naphthenic acids, petroleum sulfonic acids, oil-soluble fatty acids, etc; and ashless detergents such as the neutralization product of triethylene tetramine with an alkenyl substituted succinic anhydride having 50 carbon atoms in the alkenyl substituent and the copolymer of 5 parts of beta-diethylaminoethyl acrylate with 95 parts of dodecyl methacrylate. Oxidation-inhibitors useful in such lubricants include, e.g., basic metal petroleum sulfonates, metal phenates, amines, benzyl thiocyanates, etc. Film strength agents include, e.g., chlorinated paraffin oils containing from 20 to 70% of chlorine, chlorinated eicosane wax containing from 50 to 60% of chlorine, hexachlorodiphenyl ether, polychlorobiphenyl, etc. Oiliness agents include, e.g., methyl oleate, oleic acid, stearic acid, sulfurized sperm oil, sperm oil, corn oil, etc. Pour points depressors include, e.g., wax-alkylated naphthalene or phenanthrene, copolymer of butyl methacrylate with decyl methacrylate, etc. Foam inhibitors include, e.g., the polymeric di-alkylsilicone, poly acrylates, etc. Viscosity index improvers include, e.g., polymerized and copolymerized alkyl methacrylates, polymerized butenes, etc.

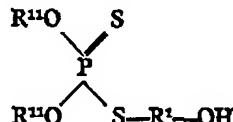
The following lubricants illustrate the utility of the phosphorus- and nitrogen-containing compositions of this invention as additives in lubricating compositions: (all percentages are by weight).

#### Lubricant A

Gear lubricant comprising SAE 90 mineral oil, 5% of a diisobutene polysulfide containing an average of 3.2 sulfur atoms per molecule prepared by the step-wise reaction of isobutene with sulfur monochloride and sodium sulfide, and 2% of the phosphorus- and nitrogen-containing product of Example 1 derived from a 2-hydroxyethyl substituted C<sub>11</sub>-C<sub>14</sub> amine mixture. This lubricant showed superior rust-inhibiting characteristics when compared with a lubricant similar in all respects except that the phosphorus- and nitrogen-containing product was derived from a C<sub>11</sub>-C<sub>14</sub> amine mixture which had not been hydroxyethyl substituted by means of ethylene oxide.

#### WHAT WE CLAIM IS:—

1. A process for preparing a phosphorus- and nitrogen-containing composition comprising forming an acidic intermediate by the reaction of a hydroxysubstituted triester of a phosphorothioic acid with an inorganic phosphorus acid, phosphorus oxide or phosphorus halide, and neutralizing a substantial portion of said acidic intermediate with a hydroxy-substituted amine.
2. The process of claim 1, wherein the inorganic phosphorus reagent is phosphorus pentoxide.
3. A process for preparing a phosphorus- and nitrogen-containing composition comprising forming an acidic intermediate by the reaction of the hydroxy-substituted triester of a phosphoro-dithioic acid having the formula



wherein R<sup>11</sup> and R<sup>1</sup> are monovalent and bivalent substantially hydrocarbon radicals respectively with phosphorus pentoxide and neutralizing a substantial proportion of said acidic intermediate with a hydroxy-substituted amine.

4. The process of claim 3, wherein R<sup>11</sup> and R<sup>1</sup> in the formula are aliphatic radicals.

5. The process of claim 4, wherein R<sup>11</sup> in the formula is an alkyl radical and R<sup>1</sup> in the formula is an alkylene radical.

6. The process of claim 3, wherein R<sup>11</sup> in the formula is an aliphatically-substituted aromatic radical and R<sup>1</sup> of the formula is a substantially aliphatic radical.

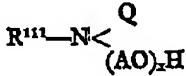
10. 7. The process of claim 6, wherein R<sup>11</sup> in the formula is an alkaryl radical and R<sup>1</sup> in the formula is an alkylene radical.

8. The process of any one of claims 3 to 7, wherein the molar ratio of the hydroxy-substituted triester of phosphorodithioic acid to phosphorus pentoxide used in forming the acidic intermediate is within the range from 2:1 to 5:1.

15. 9. The process of any one of claims 3 to 8, wherein the reaction of the hydroxy-substituted triester of a phosphorodithioic acid with phosphorus pentoxide is carried out at a temperature within the range from 50°C to 150°C.

10. 10. The process of any preceding claim, wherein the amine is a hydroxy-substituted aliphatic amine.

20. 11. The process of any preceding claim, wherein the amine has the formula.



wherein R<sup>111</sup> is a substantially hydrocarbon radical; A is a C<sub>1-5</sub> alkylene radical; x is a number from 1 to 10 inclusive; and Q is hydrogen, (AO)<sub>x</sub>H, or R<sup>111</sup>.

25. 12. The process of claim 11, wherein the amine is a N-monohydroxyalkyl substituted mono-tertiary-alkyl amine wherein the tertiary-alkyl radical contains from 11 to 24 carbon atoms.

13. A composition made by a process according to any preceding claim.

14. A lubricating composition comprising a major proportion by weight of a lubricating oil and a minor proportion by weight of a composition according to claim 13.

30. 15. A lubricating composition substantially as hereinbefore described as Lubricant A.

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